#### PAT' COOPERATION TREATY

#### To:

#### PCT

#### **NOTIFICATION OF ELECTION**

(PCT Rule 61.2)

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
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Arlington, VA 22202

in its capacity as elected Office

From the INTERNATIONAL BUREAU

**ETATS-UNIS D'AMERIQUE** 

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International application No. PCT/FI00/00487

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Applicant's or agent's file reference AH/FI991280

Priority date (day/month/year) 04 June 1999 (04.06.99)

**Applicant** 

JOHANSSON, Tor

1.	The designated Office is hereby notified of its election made:
	X in the demand filed with the International Preliminary Examining Authority on:
	28 November 2000 (28.11.00)
	in a notice effecting later election filed with the International Bureau on:
2.	The election X was
	was not
	made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Authorized officer

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### ENT COOPERATION TREATY

# **PCT**



### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

A 1:			<del></del>
Applicant's or agent's file reference AH/FI991280	FOR FURTHER ACTION		ation of Transmittal of International VExamination Report (Form PCT/IPEA/416)
International application No.	International filing date (day/me	onth/year)	Priority date (day/month/year)
PCT/FI00/00487	31.05.2000		04.06.1999
International Patent Classification (IPC) o	r national classification and IPC:	7	
C 08 J 5/18, A 22 C 1			
0 00 0 0,10, 11 22 0 1	<i>3</i> , <i>3</i>		
Applicant			
Eriksson Capital AB e	t al		
This international preliminary exa	mination report has been prepare	xd by this Inter	mational Preliminary Examining
Authority and is transmitted to the	e applicant according to Article 3	6.	
2. This REPORT consists of a total of	of 4 sheets, includ	ling this cover	sheet.
This report is also accompa			on, claims and/or drawings which have
been amended and are the b	asis for this report and/or sheets	containing rec	tifications made before this Authority
(see Rule 70.16 and Section	607 of the Administrative Instru	ections under t	he PCT).
These annexes consist of a total of	f 4 sheets.		
3. This report contains indications re	lating to the following items:		
I Basis of the report			
II Priority			
III Non-establishment of	opinion with regard to novelty, i	inventive step	and industrial applicability
IV Lack of unity of inver			
		novelty, inve	entive step or industrial applicability;
	tions supporting such statement	-	
VI Certain documents ci			
VII Certain defects in the	international application		
VIII Certain observations	on the international application		
Date of submission of the demand	Data o	f completion of	of this range
Date of submission of the demand	Date o	i completion (	or this report
28.11.2000	24 (	09.2001	
Name and mailing address of the IPEA/SE	Author	rized officer	
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3-11, 41 STOCKHOLI) Fraccimila No. 09-667, 72, 88	FATOREGES Dagi	mar Jär	vman/EO

Form PCT/IPEA/409 (cover sheet) (January 1998)

# International application No.

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

PCT/FI00/00487

I.	Basi	asis of the report	
1.	With	th regard to the elements of the international application:*	
		the international application as originally filed	
	$\overline{\boxtimes}$	the description:	
	تحا	pages 1-24	, as originally filed
		pages	, filed with the demand
		pages, fi	iled with the letter of
	$\boxtimes$	the claims:	
		pages	, as originally filed
		pages, as	amended (together with any statement) under article 19
		pages	, filed with the demand
		pages 25-28 , f	iled with the letter of 14.09.2001
	$\bowtie$	the drawings:	
		pages	, as originally filed
		pages	, filed with the demand
		pages, f	lied with the letter of
	Ш	the sequence listing part of the description:	, as originally filed
		pages	· · · · · · · · · · · · · · · · · · ·
		pages , f	, filed with the demand
3.	These	international application was filed, unless otherwise indicated under these elements were available or furnished to this Authority in the follow the language of a translation furnished for the purposes of international application (under I the language of publication of the international application (under I the language of the translation furnished for the purposes of internation 55.3).  The regard to any nucleotide and/or amino acid sequence disclosed in liminary examination was carried out on the basis of the sequence listing contained in the international application in written form.  If filed together with the international application in computer readable furnished subsequently to this Authority in written form.  If furnished subsequently to this Authority in computer readable form.	ing language which is: onal search (under Rule 23.1(b)). Rule 48.3(b)). utional preliminary examination (under Rules 55.2 and/ the international application, the international ing:
		The statement that the subsequently furnished written sequence list international application as filed has been furnished.  The statement that the information recorded in computer readable fibeen furnished.	ing does not go beyond the disclosure in the
4.		The amendments have resulted in the cancellation of:	
		the description, pages	
		the claims, Nos.	
		the drawings, sheet/fig	
5.		This report has been established as if (some of) the amendments ha beyond the disclosure as filed, as indicated in the Supplemental Bo	d not been made, since they have been considered to go x (Rule 70.2 (c)).**
*	in th	placement sheets which have been furnished to the receiving Office in this report as "originally filed" and are annexed to this report since th d 70.17).	response to an invitation under Article 14 are referred to ney do not contain amendments (Rules 70.16
**	Any i	ny replacement sheet containing such amendments must be referred to t	under item I and annexed to this report.

#### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

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٧.	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
	citations and explanations supporting such statement

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1.	Statement			
	Novelty (N)	Claims	1-24	YES
		Claims		NO
	Inventive step (IS)	Claims	1-24	YES
	,	Claims		NO NO
	Industrial applicability (IA)	Claims	1-24	YES
	, ( ·,	Claims		NO

#### 2. Citations and explanations (Rule 70.7)

Cited documents:

- 1. WO9819551 A1 ( KALLE NALO GMBH )
- 2. EP0803348 A1 ( ELF ATOCHEM S. A. )
- 3. US 5840807 A ( ALAIN FREY ET AL )
- 4. US 5888597 A ( ALAIN FREY ET AL )
- 5. WO 9907769 A2 -( ELF ATOCHEM S. A.).

Amended claims have been filed on 14 September 2001. The new claims differ from the original claims 1-26 in that the new claims 1-24 are limited to a breathable polymer casing for dry sausages, to a method for the manufacture of dry sausages and to the use of a polymer for the manufacture of breathable polymer casings for dry sausages. Moreover, the original claim 1 has been changed to a new claim 1 in which the moisture vapour transmission rate has been changed from 150 to  $500 \text{g/m}^2/24 \text{hours}$ . Original claim 2 has been changed to a new claim 2 in which the specification of the moisture vapour transmission rate has been deleted. Original claim 3 has been deleted.

The documents cited in the International Search Report represent background art.

The invention defined in claims 1 - 24 is not disclosed by any of these documents.

None of the cited documents gives any indication towards the claimed breathable polymer casing for dry sausages, method for its manufacturing and its use for the manufacture of breathable polymer casings for dry sausages. No relevant combination of the cited documents would lead a person skilled in the art to the invention defined in the claims.

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#### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

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(To be used when the space in any of the preceding boxes is not sufficient)

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Therefore, the invention defined in claims 1-24 is novel and is considered to involve an inventive step. It is also considered to be industrially applicable.

Form PCT/IPEA/409 (Supplemental Box) (January 1998)

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Claims

1. A breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.

- 2. A breathable polymer casing and/or film according to claim 1, **characterized** in that a moisture vapour transmission rate (MVTR) is equal or more than  $500 \text{ g/m}^2/24$ , preferably  $2.000 20.000 \text{ g/m}^2/24$  and that the meat product is dry sausage.
- 3. A breathable polymer casing and/or film according to claim 1, **characterized** in that a moisture vapour transmission rate (MVTR) is 150-1.000 g/m<sup>2</sup>/24 and that the meat product is cooked sausage.
- 4. A breathable polymer casing and/or film according to any one of claims 1-3, characterized in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 5. A breathable polymer casing and/or film according to any one of claims 1-4, characterized in that the thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethylene glycol blocks or polypropylene glycol blocks or polytetramethylene glycol blocks or mixtures thereof, preferably polyethylene glycol blocks.
  - 6. A breathable polymer casing and/or film according to any one of claims 1-5, **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.

7. A breathable polymer casing and/or film according to any one of claims 1-6, characterized in that the casing and/or film is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

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- 8. A breathable polymer casing and/or film according to any one of claims 1-7, characterized in that the casing and/or film is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 9. A breathable polymer casing and/or film according to any one of claims 1-8, characterized in that the casing and/or film is smokeable.
  - 10. A breathable polymer casing and/or film according to any one of claims 1-9, characterized in that the casing and/or film is resistant to deterioration by cellulolytic enzymes and that it is curvable.
  - 11. A breathable polymer casing and/or film according to any one of claims 1-10, characterized in that the meat product is fish product or ham.
- 12. A method for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing and/or film is extruded, casted or blown.
- 13. A method according to claim 12 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, **characterized** in that the casing and/or film is oriented or unoriented.
- 14. A method according to claim 12 or 13 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing comprises one or two or more layers which are extruded or coextruded and the layers comprise the same polymer or different polymers.

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15. A method according to any one of claims 10-14 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the meat product is dry sausage, cooked sausage, fish product or ham.

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- 16. Use of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.
- 17. Use according to claim 16 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that a moisture vapour transmission rate (MVTR) of the casing and/or film is equal or more than  $500 \text{ g/m}^2/24$ , preferably  $2.000 20.000 \text{ g/m}^2/24$  and that the meat product is dry sausage.
- 18. Use according to claim 16 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that a moisture vapour transmission rate (MVTR) is 150-1.000 g/m<sup>2</sup>/24 and that the meat product is cooked sausage.
- 19. Use according to any one of claims 16-18 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 20. Use according to any one of claims 16-19 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethyleneglycol blocks or polypropylene glycol or polytetramethylene glycol or mixtures thereof, preferably polyethylene glycol.

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21. Use according to any one of claims 16-20 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.

- 22. Use according to any one of claims 16-21 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.
- 23. Use according to any one of claims 16-22 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 24. Use according to any one of claims 16-23 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is smokeable.

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25. Use according to any one of claims 16-24 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is resistant to deterioration by cellulolytic enzymes and that it is curvable.

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26. Use according to any one of claims 16-25 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the meat product is fish product or ham.

#### **AMENDED CLAIMS**

[received by the International Bureau on 06 November 2000 (03.10.00); original claims-1-26 replaced by new claims 1-24 (4 pages)]

- 1. A polymer casing for dry sausages. **characterized** in that the casing comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.
- 2. A polymer casing for dry sausages according to claim 1. **characterized** in that a moisture vapour transmission rate (MVTR) is equal or more than 500 g/m<sup>2</sup>/24, preferably 2.000 20.000 g/m<sup>2</sup>/24.
  - 3. A polymer casing for dry sausages according to claim 1 or 2. **characterized** in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 4. A polymer casing for dry sausages according to any one of claims 1-3, characterized in that the thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethylene glycol blocks or polypropylene glycol blocks or polytetramethylene glycol blocks or mixtures thereof, preferably polyethylene glycol blocks.

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- 5. A polymer casing for dry sausages according to any one of claims 1-4, **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.
- 6. A breathable polymer casing for dry sausages according to any one of claims 1-5. **characterized** in that the casing is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

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- 7. A polymer casing for dry sausages according to any one of claims 1-6. **characterized** in that the casing is permeable to smoke. CO<sub>2</sub>. O<sub>2</sub> and other gases and impermeable to microbes.
- 8. A polymer casing for dry sausages according to any one of claims 1-7. **characterized** in that the casing is smokeable.
- A polymer casing for dry sausages according to any one of claims 1-8. characterized in that the casing is resistant to deterioration by cellulolytic enzymes and that it is curvable.
  - 10. A polymer casing for dry sausages according to any one of claims 1-9. **characterized** in that the dry sausage is salami-type sausage.
- 11. A method for the manufacture of dry sausages, **characterized** in that meat mass is extruded into a casing and then matured, and the casing is a polymer casing comprising thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method and that the casing is extruded, casted or blown.
  - 12. A method according to claim 11 for the manufacture of dry sausages. characterized in that the casing is oriented or unoriented.
- 25 13. A method according to claim 11 or 12 for the manufacture of dry sausages, characterized in that the casing comprises one or two or more layers which are extruded or coextruded and the layers comprise the same polymer or different polymers.
- 14. A method according to any one of claims 11-13 for the manufacture of dry sausages. **characterized** in that the dry sausage is salami-type sausage.

15. Use of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.

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16. Use according to claim 15 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that a moisture vapour transmission rate (MVTR) of the casing and/or film is equal or more than  $500 \text{ g/m}^2/24$ , preferably  $2.000 - 20.000 \text{ g/m}^2/24$ .

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- 17. Use according to claim 15 or 16 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 18. Use according to any one of claims 15-17 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethyleneglycol blocks or polypropylene glycol or polytetramethylene glycol or mixtures thereof, preferably polyethylene glycol.

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- 19. Use according to any one of claims 15-18 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.
- 20. Use according to any one of claims 15-19 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

- 21. Use according to any one of claims 15-20 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 5 22. Use according to any one of claims 15-21 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is smokeable.
  - 23. Use according to any one of claims 15-22 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is resistant to deterioration by cellulolytic enzymes and that it is curvable.
  - 24. Use according to any one of claims 15-23 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that the dry sausage is salamitype sausage.

# (19) World Intellectual Property Organization International Bureau





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- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- With international search report.
- With amended claims.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(54) Title: BREATHABLE THERMOPLASTIC POLYMER CASING FOR THE MANUFACTURE OF MEAT PRODUCTS

(57) Abstract: The invention relates to a food casing and more particularly to a breathable polymer food casing for the manufacture of meat products, such as dry sausages and cooked sausages and to a method for the manufacture thereof. Additionally, the invention relates to the use of a film or casing which is permeable to water vapour for dehydrating and/or maturing and/or smoking of meat products and more particularly to the use of films which are permeable to water and gases and which are continuous, that is to say which do not comprise perforations. The casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.



## JC10 Rec'd PCT/PTO 0 4 DEC 2001

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Breathable thermoplastic polymer casing for the manufacture of meat products

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This invention relates to a food casing and more particularly to a breathable polymer food casing for stuffing food products, such as meat products like dry sausages and cooked sausages and to a method for the manufacture thereof. Additionally, the present invention relates to the use of a film or casing which is permeable to water vapour for dehydrating and/or maturing food products and more particularly to the use of films which are permeable to water and/or smoke and which are continuous, that is to say which do not comprise perforations.

Food casings formed from synthetic materials and particularly from regenerated cellulose are widely used in the preparation of processed meat products such as sausage products and they replace earlier used casings formed from natural materials. A fibrous casing consists of a fibrous web formed into a tube and impregnated with regenerated cellulose. Differences in meat products, sausage recipes and modes of processing make it difficult to provide a casing that is suitable for all types of sausage products.

Dry sausages, such as salami and the like, are usually processed by maturing for extended periods of time rather than cooking. The manufacture and maturing process of dry sausages is a complex interaction of so-called internal control variables e.g. recipe and external control variables e.g. climate. The internal control variables comprise common salt and sugar content, fat content, degree of comminution, casing and starter cultures. The external control variables comprise relative humidity, temperature and air velocity. A bacterial pure culture i.e. a starter culture is used to ensure the designed colour formation and to produce acids, mainly lactic acid that lower the pH value. Curing takes usually place in a smoke oven, often called a climatic chamber. The ability of meat to bind its own water is weakened because of

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the lowered pH value and because the relatively high salt content controls the lowering of the pH value. As a result of the lowered pH value, the salt content and the external control variables, meat products like sausages mature. Thus water is released from the meat, then it is diffused from the core of the sausage to the surface and finally evaporated through the casing. In order to permit moisture to be removed and to enable smoke to be accessible to the sausage, the casing must be permeable to moisture and gases. Casings of the fibrous type are commercially available for the processing of a variety of dry sausages.

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EP 850,567 discloses a process for the manufacture of cellulose containing casings, which are suitable for sausages such as salami. The conditions, especially conditions after maturing of dry sausages are sometimes found to result in the growth of undesirable mold and fungi on the tubular, fibrous cellulosic casings producing cellulolytic enzymes that cause deterioration of the casings and which can render the sausage product unsaleable. Also the removal of possible extrenuous material is difficult from the fibrous casings because the use of water is undesirable in connection with fibrous casings.

It is sometimes difficult to peel the fibrous casing from the sausage without breaking the casing and at worst, only separate pieces can be pulled off. The manufacturing process of fibrous casings requires several different steps and especially the problems associated with environmental aspects, such as emissions of volatile organic compounds, make the process for the manufacture of fibrous casings unattractive. When fibrous casings are used, usually an adhesion substance, such as epichlorohydrine, is needed in order to achieve the adhesion of the meat mass to the inner surface of the casing.

Solutions to the problems associated with fibrous casings in connection with dry sausages have been proposed in several publications.

US 4,780,326 discloses a composition for making pigmented protective coatings on meat products, which coatings are based on acetylated monoglycerides and cellulose

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esters with additional synthetic waxes and pigments. Raw sausages are dipped into the melted composition and allowed to be dried.

US 3,935,320 discloses a tubular cellulosic casing with a kationic thermosetting resin coating which exhibits resistance to degradation by cellulolytic enzymes.

Traditional plastic casings which comprise polyester or nylon are widely used in the manufacture of stuffed food products, like cooked sausages and other moist type of sausages, which require that moisture is retained during processing and storage, thus necessitating the use of casings which are substantially impermeable. It is evident that moisture and smoke impermeable plastic casings are not suitable for the manufacture of meat products like dry sausages, such as salami or pepperoni, where moisture, smoke and gas permeability are very important features of the casings. Commonly, dry sausages are manufactured into permeable fibrous casings, collagen casings, cellophane casings or natural casings.

Meat products and particularly cooked sausages which are optionally smoked are commonly manufactures into non-edible collagen casings. Collagen originates from bovine and thus there is a potential risk for BSE and bovine induced allergy. Collagen casings have weak mechanical properties and because collagen originates from different animal sources the quality of collagen varies and effects the pealability of the sausages. The use of collagen casings in the manufacture of meat products requires careful handling. Before the manufacture of sausages collagen casings are usually treated with saline water, which has a corroding effect on the manufacturing equipment and additionally this is a potential risk for bacterial contamination.

Based on the above, it can be seen that there exists a need for a casing especially suitable for stuffed meat products, such as dry sausages and cooked sausages, which casing is easy, environmentally safe and acceptable to manufacture and which exhibits required moisture, smoke and gas permeability.

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The prior art has disclosed films which are leaktight to liquid water and permeable to water vapour. Provision was first of all made for microperforated polyethylene films, the holes of which are sufficiently small to prevent the passage of water drops and sufficiently large to allow the passage of water vapour. As regards the polyethylene part, it is leaktight to liquid water and to water vapour. These films have the disadvantage of not keeping out bacteria or viruses.

EP 378,015 discloses films composed of a copolymer with polyamide blocks and polyether blocks. These films are continuous, that is to say that they do not have perforations, they are leaktight to liquid water and allow the passage of water vapour. Depending on the nature of the polyether, the moisture vapour transmission rate (MVTR) (also known as MWTR for Moist Water Transmission Rate) is higher or lower. The use was disclosed of these films to protect insulating materials, which are under the roofs of houses; humidity is lost and the water, which might infiltrate under the tiles or the slates cannot wet the insulating materials.

EP 688,826 discloses films composed of copolymers with polyether blocks as a mixture with copolymers of ethylene and of an alkyl (meth)acrylate. They are leaktight to liquid water and permeable to water vapour and, as regards copolymers with polyamide blocks and polyether blocks, they exhibit the advantage with respect to the preceding prior art (i) of having the same permeability for a lower water uptake, (ii) of being readily extrudable and (iii) of being able to be easily hot-bonded to a woven or non-woven.

- EP 737,709 discloses packagings composed of a film made of copolymer with polyamide blocks and polyether blocks; they have the property of being permeable not only to water vapour but also to oxygen, to CO<sub>2</sub> and to ethylene. These packagings make possible the preservation of freshly harvested fruit and vegetables.
- 30 EP 803,348 discloses packagings composed of two layers of copolymers with polyether blocks, one highly permeable to water vapour and the other weakly permeable. This technique makes it possible to prevent the presence of condensation

within the packaging. The copolymers with polyether blocks are advantageously chosen from polyether-polyamide block copolymers, polyether-polyester block copolymers and polyether-urethanes.

WO 98/26004 discloses packagings composed of a film made of a mixture (i) of a copolymer with polyether blocks, (ii) of a polyethylene with a relative density of less than 0.91 and (iii) of a compatibilizing agent. By adjusting the proportions of the various constituents, films are obtained which have specific values of permeability to water vapour, to oxygen and to CO<sub>2</sub>. These different films are of use in different kinds of preservation.

Patent EP 829,506 discloses other films composed of a polyurethane, a copolymer with polyamide blocks and polyether blocks having been added to this polyurethane; this film is permeable to water vapour and impermeable to liquid water.

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Patent EP 842,969 discloses films composed of a mixture (i) of polyamide, (ii) of a copolymer with polyamide blocks and polyether blocks, and (iii) of an optionally functionalized polyolefin, the proportion by weight of (i) being less than 50% and the proportion of (i)+(ii) being greater than 50%. This film is permeable to water vapour and impermeable to liquid water.

Patent WO 99/07769 discloses masterbatches (i) of copolymer with polyamide blocks and polyether blocks, (ii) of a functional copolymer, such as a styrene-maleic anhydride, and (iii) of a polyolefin which are intended to be added to polyolefins. The resulting mixture is used to prepare films which are permeable to water vapour, to CO<sub>2</sub> and to oxygen and impermeable to liquid water.

Patent EP 848,019 discloses films composed of a copolymer of ethylene and of a polyethylene glycol (meth)acrylate. These films are permeable to water vapour and impermeable to liquid water.

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Patent EP 476,963 discloses films composed of a mixture (i) of a copolymer with polyamide blocks and polyether blocks which are hydrophilic, (ii) of a hydrophobic polymer which can be the preceding copolymer but with hydrophobic polyether blocks or a polyamide or a polyurethane, and (iii) optionally of a compatibilizing agent. The film is permeable to water vapour and impermeable to liquid water and has a low water uptake.

Patent EP 91,800 discloses dressings based on a film composed of a copolymer with polyamide blocks and polyether blocks which film is permeable to water vapour and which keeps out bacteria. This dressing is used to protect, from infections, wounds which have not yet healed while drying them but while not drying them too quickly. This is because, if drying is too fast, healing takes place while the wound is still suppurating.

The prior art has not disclosed the dehydration and/or maturing and/or smoking of meat products using a continuous film as a packaging or casing.

The object of the invention is to provide a moisture (water vapour), smoke and gas permeable, breathable polymer casing and/or film for the manufacture of meat products like sausages and ham. A further object of the invention is to provide a method for the manufacture of such casings and/or film. A further object of the invention is the use of a polymer for the manufacture of a moisture and gas and smoke permeable, continuos casing and/or film for the manufacture of stuffed food products, such as meat products, like dry sausages, cooked sausages and ham.

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Characteristic features of the casing and/or film, of the method for the manufacture thereof and of the use of the casing and/or film are stated in the claims.

The objects of the invention are achieved and the disadvantages of the films and casings according to the prior art are avoided or significantly reduced with the casing and/or film and the method according to the invention. The invention relates particularly to meat products, which have to be matured and/or completely or

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partially dehydrated and/or smoked, the dehydration constituting a stage in their preparation. It concerns, for example, foodstuffs, such as meat products like dry sausages, cooked sausages, ham and fish products. The present invention also relates to the use of a continuous packaging film or casing which is permeable to water vapour and impermeable to liquid water for completely or partially dehydrating and/or maturing and/or smoking of food products. The term "continuous" means that the film or casing is not perforated.

It has been surprisingly found that casings based on certain polymers can be used in the manufacture of special types of food products, which require moisture (water vapour) permeability, smoke permeability and gas permeability of the casings. Especially suitable polymers are thermoplastic polymers made of flexible polymers and rigid polyamides such as polyether block amides. The thermoplastic polymers are breathable to water vapour and they are also permeable to other gases, surprisingly such as smoke, CO<sub>2</sub> and O<sub>2</sub>. On the other hand, they are impermeable to microbes thus keeping out bacteria and viruses. Casings and films manufactured from the thermoplastic polymers have good mechanical properties such as tensile strength, elongation at brake, a good smooth finish, and they are resistant to the hydrolysis and deterioration by cellulolytic enzymes. The casings and films can be manufactured into desired forms, such as tubular casings, by extrusion methods using any suitable extrusion equipment known in the art. The casing can also be manufactured by blowing or casting films, which can be sealed to any desired form. The casing or film can be oriented or unoriented and it can be manufactured as a single layer casing or as a multilayer casing with two or more layers. The casings which are preferably oriented may also be curved by stretching and/or shrinking when curved sausages are desired. The multilayer casing or film can be preferably coextruded, comprising the same polymer or a different polymer in each layer or combinations of polymers, thus making it possible to manufacture casings with varying moisture permeability. Additives, such as antiblocking agents, like silica, pigments and other additives known in the art, such as plasticizers, antioxidants or UV stabilizers, may be incorporated into the casings or films or used in connection with them.

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A suitable thermoplastic polymer is a polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m²/24 hours, when measured using the ASTM E96 BW method. For dry sausages like salami-type sausage the preferable moisture vapour transmission rate is equal or more than 500 g/m²/24 hours and more preferably 2.000 - 20.000 g/m²/24 hours. Dry sausages are conveniently matured and optionally smoked in said polymer casings. For cooked sausages like bologna-type sausage the preferable moisture vapour transmission rate is equal or more than 150 g/m²/24 hours and preferably 150 - 1.000 g/m²/24 hours. The sausages may optionally be smoked in said casings. The moisture, smoke and gas permeability of the casing can be selected depending on the sausage which is manufactured.

The film or casing is advantageously based on a polymer having polyether chains, it being possible for these chains to be side chains (copolymer B) or to be blocks (or sequences) in the main chain (copolymer A) or to be present as side chains or as blocks.

Mention may be made, as an example of a polymer having polyether side chains, of copolymers of ethylene and of a polyalkylene glycol (meth)acrylate, such as those disclosed in Application EP 848,019, the contents of which are incorporated in the present application.

Mention may be made, as an example of a polymer A having polyether blocks, of the copolymer (A) of Application WO 98/26004 which means a block copolymer in which polyoxyalkylene chains and other polymer chains are linked together, or a polymer in which polyoxyalkylene chains are connected together via coupling regions.

The polyether blocks comprise alkylene oxide units, which can be chosen from ethylene oxide, propylene oxide and -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-. The permeability

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increases with the proportion of polyether and with its nature. The greater the amount of polyethylene glycol, the greater the permeability to water vapour.

The polyether blocks can represent 5 to 85% by weight of (A). The polyether blocks can comprise other units than ethylene oxide units, such as, for example, propylene oxide or polytetrahydrofuran, which results in polytetramethylene glycol linkages. It is also possible simultaneously to use PEG blocks, that is to say those composed of ethylene oxide units, PPG blocks, that is to say those composed of propylene oxide units, and PTMG blocks, that is to say those composed of tetramethylene glycol units, also known as polytetrahydrofuran blocks. Use is advantageously made of PEG blocks or of blocks obtained by oxyethylation of bisphenols, such as, for example, bisphenol A. The latter products are disclosed in Patent EP 613,919. The amount of polyether blocks in (A) is preferably from 10 to 50% by weight of (B).

Advantageously, (A) is a copolymer with polyamide blocks and polyether blocks.

Polymers with polyamide blocks and polyether blocks result from the copolycondensation of polyamide sequences comprising reactive ends with polyether sequences comprising reactive ends, such as, inter alia:

- polyamide sequences comprising diamine chain ends with polyoxyalkylene sequences comprising dicarboxylic chain ends,
  - 2) polyamide sequences comprising dicarboxylic chain ends with polyoxyalkylene sequences comprising diamine chain ends obtained by cyanoethylation and hydrogenation of  $\alpha$ , $\omega$ -dihydroxylated aliphatic polyoxy-alkylene sequences, known as polyetherdiols,
  - 3) polyamide sequences comprising dicarboxylic chain ends with polyetherdiols, the products obtained being, in this specific case, polyetheresteramides.

Polyamide sequences comprising dicarboxylic chain ends originate, for example, 30 from the condensation of α,ω-aminocarboxylic acids, of lactams or of dicarboxylic

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acids and diamines in the presence of a chain-limiting dicarboxylic acid. The polyamide blocks are advantageously made of polyamide-12.

The number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000. The mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.

The polyamide blocks and polyether blocks can also comprise randomly distributed units. These polymers can be prepared by the simultaneous reaction of the polyether and of the precursors of the polyamide blocks.

For example, polyetherdiol, a lactam (or an  $\alpha,\omega$ -amino acid) and a chain-limiting diacid can be reacted in the presence of a small amount of water. A polymer is obtained which has essentially polyether blocks and polyamide blocks of very variable length but also the various reactants, which have reacted randomly, which are statistically distributed along the polymer chain.

These polymers with polyamide blocks and polyether blocks, whether they originate from the copolycondensation of polyamide and polyether sequences prepared beforehand or from a one-stage reaction, exhibit, for example, Shore D hardnesses which can be between 20 and 75 and advantageously between 30 and 70 and an intrinsic viscosity between 0.8 and 2.5, measured in meta-cresol at 25°C for a starting concentration of 0.8 g/100 ml.

Whether the polyether blocks derive from polyethylene glycol, polypropylene glycol or polytetramethylene glycol, they are either used as is and copolycondensed with polyamide blocks comprising carboxylic ends or they are aminated, in order to be converted into polyetherdiamines, and condensed with polyamide blocks comprising carboxylic ends. They can also be mixed with polyamide precursors and a chain-limiting agent in order to form polymers with polyamide blocks and polyether blocks having statistically distributed units.

The polyether can be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG) or a polytetramethylene glycol (PTMG). The latter is also known as polytetrahydrofuran (PTHF).

Whether the polyether blocks are in the chain of the polymer with polyamide blocks and polyether blocks in the form of diols or of diamines, they are known for simplicity as PEG blocks or PPG blocks or PTMG blocks.

It would not be departing from the scope of the invention if the polyether blocks comprised different units, such as units derived from ethylene glycol (-OC<sub>2</sub>H<sub>4</sub>-), from propylene glycol

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or from tetramethylene glycol (-O-(CH<sub>2</sub>)<sub>4</sub>-).

The polymer with polyamide blocks and polyether blocks preferably comprises a single type of polyamide block and a single type of polyether block. Use is advantageously made of polymers with PA-12 blocks and PEG blocks and of polymers with PA-12 blocks and PTMG blocks.

Polymers with PEG blocks have a much greater permeability to water vapour than that of polymers with PTMG blocks.

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Use may also be made of a mixture of these two polymers with polyamide blocks and polyether blocks.

The polymer with polyamide blocks and polyether blocks is advantageously such that the polyamide is the major constituent by weight, that is to say that the amount of polyamide which is in the form of blocks and that which is optionally statistically distributed in the chain represents 40% by weight or more of the polymer with polyamide blocks and polyether blocks. The amount of polyamide and the amount of

polyether are advantageously in the ratio (polyamide/polyether) 1/1 to 3/1 and preferably:

The films of the invention have a thickness, for example, of between 10 and 150 µm.

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The copolymers (A) and (B) can also be mixed with two or more polymers, like polyamides or polyolefins, having different types and/or ratios of soft/hard segments in each resin, or again there may be used blends with other resins providing that the amount is within a range such that the objectives of the present invention are realised.

The manufacturing process of the films or casings according to the invention is simple and it presents no environmental problems related to emissions of volatile organic compounds or undesirable smells. The polymer leftovers from the manufacturing process can be recycled to the process and practically no waste is formed. Meat products requiring moisture and gas permeability of the casing or film, such as dry sausages like salamis, pepperonis and the like, can easily be manufactured in the casings or films according to the invention. The casings or films can be in a tubular form which is sealable with metal clips or other known method or they can be heat-sealed, or they can be in flat film that is sealable to a desired form.

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Another advantage of the invention relates to substances, which have to be packaged in order to be shaped during their preparation, this packaging also serving, in the following stage, subsequently to completely or partially dehydrate them. Thus meat products, such as salami, may be manufactured by extrusion of a meat mass into a tube, the dehydration and/or maturing subsequently having to be provided by this tube. Surprisingly, the dry sausages packed in casings or films according to the invention are readily smokeable just like dry sausages in conventional fibrous casings. The food product may be subjected to smoke or it may also be matured and/or dehydrated without smoke.

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In the manufacture of dry sausages like salami no adhesion substances like epichlorohydrine is needed. The sausages can be cleaned and rinsed with water if needed without harming the product. The moisture and gas permeability of the casings or films can be varied depending on the food product. The thermoplastic polymer casings and films according to the invention are easily peelable leaving a smooth surface on the meat product like sausage.

Surprisingly meat products, particularly dry sausages and cooked sausages, may conveniently be manufactured into polymer casings according to the invention, wherein the moisture vapour transmission rate is equal or more than 150 g/m²/24 hours. These sausages are smokeable and the smoked and peeled product has similar taste, odour and colour when compared to similar products manufactured into conventional casings. Also the concentrations of certain major smoke components, of guaiacol and m-cresol and p-cresol, are at the same levels in sausages manufactured into the casings according to the invention when compared to sausages manufactured into traditional collagen casings. Curved sausages can be manufactured by using oriented casing material. Meat products, particularly sausages manufactured into the casings according to the invention require no further re-packaging because the casing material is microbe proof. Additionally the casing resists action of cellulolytic enzymes and thus problems of conventional cellulose casings are also avoided.

The invention is further illustrated in the following examples, which however are not meant to limit the scope of the invention.

#### Example 1

Salami type sausage was manufactured using an extruded thermoplastic polymer casing comprising copolymer with polyamide 12 blocks with molecular weight of 4500 and with PEG blocks with a molecular weight of 1500, and MFI between 4 and 8 (235 C under 1 kg), with an extrusion diameter of 75 mm and a moisture vapour transmission rate MVTR of approximately 500 g/m<sup>2</sup>/24 hours. As a reference casing

a conventional fibrous casing with an extrusion diameter of 70 mm was used. The following experimental parameters expressing the quality of dry sausages were monitored during the maturing process:

- 1. Acidity degree (pH value)
- 5 2. Firmness

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3. Weight loss

The pH values of the sausages were measured every day during the first three days and then after the sausages had matured. Firmness was controlled to ensure that a drying ring had not occurred and that the sausages were acceptable. The weight loss of dry sausage during ripening is normally expressed as a percentage, the weight determined at the time of sampling being related to the initial weight on the day of manufacture. After 60 hours, the pH value of the test sausage varied between 4.8 and 4.9 and the pH value of the reference sausage varied between 4.7 and 4.8. The typical red colour for a dry sausage was developed in a normal way within 36 hours.

The weight loss is presented in the following Table 1.

Table 1

Weight loss of salami sausage manufactured in thermoplastic polymer casing.

Time (days)	Weight loss (%)
2.5	2.9
6.5	8.2
7.5*	10.3
10.5	17.5
13.5	21.4
15.5	23.8
17.5	25.3
20.5	27.7
24.5	30

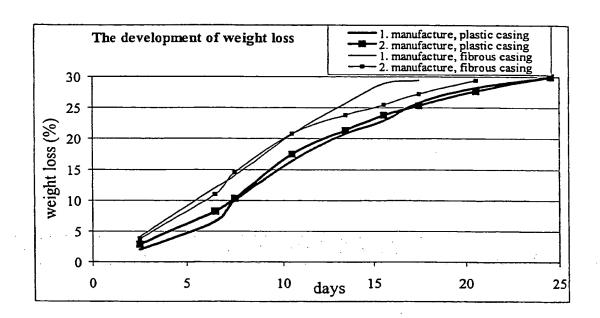
\* after maturing warehousing started

The maturing time of 24—25 days to the weight loss of 30 % is a normal time for a dry sausage with this diameter.

The weight loss of sausages in fibrous casings and in thermoplastic polymer (plastic) casings is presented in the following diagram 1.

#### Diagram 1.

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Table 2 shows the consistence (hardness) of the sausage during maturing. The measuring of consistence was performed in order to ensure that a so-called drying-ring was not formed to the product during maturing. Hardness is measured by pressing the measuring head (Ø 10 mm) to the depth of 10 mm with respect to the horizontal direction of the peeled sausage. The numerical value obtained expresses the magnitude of force required to press the measuring head to a specified depth. Three parallel measurements were performed.

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Table 2

Development of consistence (hardness)

Weight	Plastic casing, 1	Fibrous casing, 1	Plastic casing, 2	Fibrous casing, 2
loss, %				
20	5.7–6.0 kg	6.6–7.4 kg	6.4 kg	6.8 kg
25	not measured	not measured	6.8–8.4 kg	7.2–8.2 kg
30	11.5 kg	12.5 kg	8.5–9.8 kg	10 kg

The salami sausage in the thermoplastic polymer casing was more easily peelable than the corresponding salami sausage in the fibrous casing. The taste and the flavour of the ready-made salami packed in the polymer were typical of a salami of good quality.

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#### Example 2

# Smokeability-properties of four different plastic casings

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Both smoke flavour and color are formed by combined effect of many agents/substances and by their reactions with the product itself. Smoke flavour and color do not necessarily form by influence of the same factors, and certain factors have also synergetic properties. Several hundreds of different compounds are detectable in curing smoke. Those compounds can be identified by usings gas chromatography in connection with mass spectrometry. However, it is not completely evident, which components of curing smoke form the smoke flavour exactly. The phenolic compounds guaiacol and meta- and para-cresol are regarded as the most significant factors as products' flavour's point of view. Thus the best method to evaluate the *smokyness* of the product is sensory evaluation.

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Smoking provides the following effects: flavouring, coloring, preserving by anti-oxidative and antimicrobial action and formation of a secondary skin.

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Table 3

Smokeability means here the smoke-permeability properties of the casing and term smokyness refers to smoky taste, aroma and color of the final, peeled product. The smokeability-properties of four different plastic casings were compared with a non-edible collagen casing.

Four different plastic casings were examined. As a reference sample a commonly used, non-edible collagen casing was used. As another comparison sample in sensory evaluation a commercial product (bologna-type sausage, manufactured by Atria Oyj, Finland) prepared into impermeable plastic casing was used. Results are presented in table 3.

Casings examined and their moisture vapour transmission rate.

Casing	Material	Moisture vapour transmission rate g/m <sup>2</sup> /24 hours (23°C, rH 50%)
1	plastic	850
2	plastic	3000
3	plastic	50
4	plastic	2000
. 5	collagen, non-edible	>3000

#### Processing of the sausages

The sausage mix was stubbed into the sample casings and the sausages were smoked and cooked by the program characteristic to smoked sausages. Smoking process was so called hot smoke processing (50-85°C) (Tóth & Potthast, 1984). After cooking and cooling the sausages were vacuum-packed and cold-storaged at 3.5°C.

#### Sausage mix:

Ingredients	w/w %	
pork meat	75.2	
potato starch	1.5	
soya protein	1.0	
salt	1.7	
spices	0.24	
stabilizer		
antioxidant		· · · · · · · · · · · · · · · · · · ·
preservative		
water	20	
total	100	

#### 5 Smoking process:

Smoking process	°C	rH	min.	
smoking 1	70	0	6	
smoking 2	70	55	6	
total			. 12	

Smoke was produced by a so called external smoke generator. The smoke generator works by the programming of the steam-cook house.

#### Sensory evaluation

The sensory evaluation of the products was carried out after two and after three days from processing.

The panel evaluated *smokyness* (smoke's intensity of taste and aroma) from the peeled sausages.

The evaluation method used was so called graphic method (estimation for intensity), in which the evaluators marked their opinion of the product's intensity of smoky taste or aroma on the 150 mm line segment. The line segment was anchored from it's ends by the terms that described the studied property (aroma: no smoky aroma intense smoky aroma; taste; no smoky taste - intense smoky taste).

#### 10 Results

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#### First day

The results of evaluation between samples (casings) examined are shown in Table 4. Correlation between individual properties are shown in Table 5.

Table 4

Points of sensory evaluation for each sample (casing). The casings that are marked by the same character (a or b) do not have statistical difference (p < 0.001) regarding the property examined.

Casing	Plastic	Plastic	Plastic	Plastic
Moisture vapour transmission rate g/m²/24 hours (23°C, rH 50 %)	3000	850	200	50
Aroma	93.0a	79.8a	27.3b	22.4b
Taste	93.1a	94.7a	37.4b	42.9b

Table 5

## Correlation between individual properties (vp = moisture vapour transmission rate)

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Properties	Correlation		
Aroma / taste	0.98		
Aroma / vp	0.85		
Taste / vp	0.75		

#### Second day

The results of evaluation between samples (casings) examined are shown in Table 6.

Correlations between individual properties are shown in Table 7.

#### Table 6

Points of sensory evaluation for each sample (casing). The casings that are marked by the same character (a or b) do not have statistical difference (p < 0.05) regarding the property that was examined.

Casing	Collagen	Plastic	Plastic	Plastic	Plastic
Moisture vapour transmission rate g/m²/24 hours (23°C, rH 50 %)	-	3000	850	200	50
Aroma	100.1a	67.6b	56.0b	31.3c	24.0c
Taste	92.9a	94.1a	53.5b	42.2bc	30.1c

Table 7

### Correlation between individual properties (vp = moisture vapour transmission rate)

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Properties	Correlation	
Aroma / taste	0.90	
Aroma / vp	0.89	
Taste / vp	0.99	

It can be seen from the results that the *smokyness* of the products increased as the moisture vapour transmission rate (vp) of the casings increased. As the moisture vapour transmission rate of the casing was minor (200 and 50) the *smokyness* of the product was also minor. As the moisture vapour transmission rate was 850 g/m²/24 hours the product's *smokyness* was already eminent, and it further increased as the moisture vapour transmission rate was 3000 g/m²/24 hours. As the moisture vapour transmission rate was 3000 g/m²/24 hours the product could be considered as "normal smoky".

A significant correlation was found between vp-value and *smokyness* (on an average 0.88).

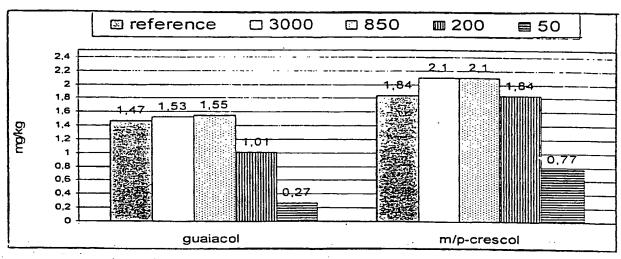
Differences between the samples were examined by the analysis of variance (LSD-method). Correlation between individual factors was examined.

#### Determination of guaiacol- and m/p-cresol-contents

25 \_ The method of analysis used was a GC/MS-method.

The contents of guaiacol and m/p-cresol in the products are shown in diagram 2.

Diagram 2.



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Guaiacol- and m/p-cresol-contens in products. Reference = sausage prepared into collagen casing. 3000, 850, 200 and 50 indicate the moisture vapour transmission rate,  $g/m^2/24$  hr (23°C, rH 50 %), of the casings.

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In the sausage prepared into casing with vp-value of 50 g/m²/24 hours the guaiacol and m/p-cresol-contents were clearly on lower level than in the others. In the sausage prepared into casing with vp-value of 200 g/m²/24 hours the guaiacol-content was lower than in the reference (collagen) sausage, but the m/p-cresol-content was on the same level. In the sausages prepared into casings with vp-values of 850 or 3000 g/m²/24 hours the guaiacol- and m/p-cresol-contents were on the same level or even higher than in reference.

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At the low moisture vapour transmission rate of 50 g/m<sup>2</sup>/24 hours the product's guaiacol and m/p-cresol-contents remain considerably lower than at the moisture vapour transmission rate of 200 g/m<sup>2</sup>/24 hours. Because at the level of 200

g/m<sup>2</sup>/24 hours the guaiacol and m/p-cresol-contents are already quite near the contents of the reference, it can be concluded that between the moisture vapour transmission rate of 50-200 g/m<sup>2</sup>/24 hours the product's guaiacol and m/p-cresolcontents can be affected quite remarkable.

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At the moisture vapour transmission rate of 200 g/m<sup>2</sup>/24 hours or more, by increasing permeability, a product's guaiacol and m/p-cresol-contents can not be affected as much as on the lower permeability levels.

10 The results of analysis of guaiacol and m/p-cresol-contents support the results of sensory evaluation. Comparing the results of chemical analysis and sensory evaluation it can, however, be observed that guaiacol and m/p-cresol are not the only compounds in curing smoke that affect product's aroma and taste, because in sensory evaluation also with the product prepared into casing with vp-value of 200 g/m<sup>2</sup>/24 hours the *smokyness* was considered as minor.

The smokyness of the product can be pointed out to be dependent on vapour permeability of the plastic casing used in particular conditions.

#### Claims

- 1. A breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.
- 2. A breathable polymer casing and/or film according to claim 1, characterized in that a moisture vapour transmission rate (MVTR) is equal or more than 500 g/m $^2$ /24, preferably 2.000 20.000 g/m $^2$ /24 and that the meat product is dry sausage.
- 3. A breathable polymer casing and/or film according to claim 1, characterized in that a moisture vapour transmission rate (MVTR) is 150-1.000 g/m<sup>2</sup>/24 and that the meat product is cooked sausage.

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- 4. A breathable polymer casing and/or film according to any one of claims 1-3, characterized in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 5. A breathable polymer casing and/or film according to any one of claims 1-4, characterized in that the thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethylene glycol blocks or polypropylene glycol blocks or polytetramethylene glycol blocks or mixtures thereof, preferably

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polyethylene glycol blocks.

6. A breathable polymer casing and/or film according to any one of claims 1-5, characterized in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.

7. A breathable polymer casing and/or film according to any one of claims 1-6, characterized in that the casing and/or film is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

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- 8. A breathable polymer casing and/or film according to any one of claims 1-7, characterized in that the casing and/or film is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 9. A breathable polymer casing and/or film according to any one of claims 1-8, characterized in that the casing and/or film is smokeable.
  - 10. A breathable polymer casing and/or film according to any one of claims 1-9, characterized in that the casing and/or film is resistant to deterioration by cellulolytic enzymes and that it is curvable.
  - 11. A breathable polymer casing and/or film according to any one of claims 1-10, characterized in that the meat product is fish product or ham.
- 12. A method for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, **characterized** in that the casing and/or film is extruded, casted or blown.
- 13. A method according to claim 12 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing and/or film is oriented or unoriented.
  - 14. A method according to claim 12 or 13 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the casing comprises one or two or more layers which are extruded or coextruded and the layers comprise the same polymer or different polymers.

15. A method according to any one of claims 10-14 for the manufacture of a breathable polymer casing and/or film for the manufacture of meat products, characterized in that the meat product is dry sausage, cooked sausage, fish product or ham.

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- 16. Use of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.
- 17. Use according to claim 16 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that a moisture vapour transmission rate (MVTR) of the casing and/or film is equal or more than 500 g/m<sup>2</sup>/24, preferably 2.000 20.000 g/m<sup>2</sup>/24 and that the meat product is dry sausage.
  - 18. Use according to claim 16 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that a moisture vapour transmission rate (MVTR) is 150-1.000 g/m<sup>2</sup>/24 and that the meat product is cooked sausage.
  - 19. Use according to any one of claims 16-18 of a polymer for the manufacture of breathable casings and/or films of meat products, characterized in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
  - 20. Use according to any one of claims 16-19 of a polymer for the manufacture of breathable casings and/or films of meat products, characterized in that thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethyleneglycol blocks or polypropylene glycol or polytetramethylene glycol or mixtures thereof, preferably polyethylene glycol.

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- 21. Use according to any one of claims 16-20 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.
- 22. Use according to any one of claims 16-21 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.
- 23. Use according to any one of claims 16-22 of a polymer for the manufacture of breathable casings and/or films of meat products, characterized in that the casing and/or film is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 24. Use according to any one of claims 16-23 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is smokeable.
- 25. Use according to any one of claims 16-24 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the casing and/or film is resistant to deterioration by cellulolytic enzymes and that it is curvable.
- 26. Use according to any one of claims 16-25 of a polymer for the manufacture of breathable casings and/or films of meat products, **characterized** in that the meat product is fish product or ham.

#### AMENDED CLAIMS

[received by the International Bureau on 06 November 2000 (03.10.00); original claims-1-26 replaced by new claims 1-24 (4 pages)]

- 1. A polymer casing for dry sausages. **characterized** in that the casing comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.
- 2. A polymer casing for dry sausages according to claim 1. **characterized** in that a moisture vapour transmission rate (MVTR) is equal or more than 500 g/m<sup>2</sup>/24. preferably 2.000 20.000 g/m<sup>2</sup>/24.
  - 3. A polymer casing for dry sausages according to claim 1 or 2. **characterized** in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.
- 4. A polymer casing for dry sausages according to any one of claims 1-3, characterized in that the thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethylene glycol blocks or polypropylene glycol blocks or polytetramethylene glycol blocks or mixtures thereof, preferably polyethylene glycol blocks.

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- 5. A polymer casing for dry sausages according to any one of claims 1-4, characterized in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.
- 6. A breathable polymer casing for dry sausages according to any one of claims 1-5. characterized in that the casing is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

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- 7. A polymer casing for dry sausages according to any one of claims 1-6. characterized in that the casing is permeable to smoke. CO<sub>2</sub>. O<sub>2</sub> and other gases and impermeable to microbes.
- 8. A polymer casing for dry sausages according to any one of claims 1-7. characterized in that the casing is smokeable.
  - 9. A polymer casing for dry sausages according to any one of claims 1-8, characterized in that the casing is resistant to deterioration by cellulolytic enzymes and that it is curvable.
  - 10. A polymer casing for dry sausages according to any one of claims 1-9. characterized in that the dry sausage is salami-type sausage.
- 11. A method for the manufacture of dry sausages, **characterized** in that meat mass is extruded into a casing and then matured, and the casing is a polymer casing comprising thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m²/24 hours measured by the ASTM E96 BW method and that the casing is extruded, casted or blown.
  - 12. A method according to claim 11 for the manufacture of dry sausages. characterized in that the casing is oriented or unoriented.
- 25 13. A method according to claim 11 or 12 for the manufacture of dry sausages, characterized in that the casing comprises one or two or more layers which are extruded or coextruded and the layers comprise the same polymer or different polymers.
- 14. A method according to any one of claims 11-13 for the manufacture of dry sausages, characterized in that the dry sausage is salami-type sausage.

## AMENDED SHEET (ARTICLE 19)



15. Use of a polymer for the manufacture of polymer casings for dry sausages, characterized in that the casing comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m<sup>2</sup>/24 hours measured by the ASTM E96 BW method.

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16. Use according to claim 15 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that a moisture vapour transmission rate (MVTR) of the casing and/or film is equal or more than  $500 \text{ g/m}^2/24$ , preferably  $2.000 - 20.000 \text{ g/m}^2/24$ .

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17. Use according to claim 15 or 16 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the thermoplastic polymer comprises polyamide blocks and polyether blocks.

18. Use according to any one of claims 15-17 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that thermoplastic polymer comprises a polymer with polyamide 12 blocks and with polyethyleneglycol blocks or polypropylene glycol or polytetramethylene glycol or mixtures thereof, preferably polyethylene glycol.

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- 19. Use according to any one of claims 15-18 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the number-average molar mass of the polyamide sequences is between 300 and 15,000 and preferably between 600 and 5000, and the mass of the polyether sequences is between 100 and 6000 and preferably between 200 and 3000.
- 20. Use according to any one of claims 15-19 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is oriented or unoriented and it comprises one or two or more layers, and the layers comprise the same polymer or different polymers.

- 21. Use according to any one of claims 15-20 of a polymer for the manufacture of polymer casings for dry sausages. **characterized** in that the casing is permeable to smoke, CO<sub>2</sub>, O<sub>2</sub> and other gases and impermeable to microbes.
- 5 22. Use according to any one of claims 15-21 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that the casing is smokeable.
  - 23. Use according to any one of claims 15-22 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that the casing is resistant to deterioration by cellulolytic enzymes and that it is curvable.
    - 24. Use according to any one of claims 15-23 of a polymer for the manufacture of polymer casings for dry sausages, **characterized** in that the dry sausage is salamitype sausage.



#### A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08J 5/18, A22C 13/00
According to International Patent Classification (IPC) or to both national classification and IPC

#### FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08J, A22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

#### B51, WPI

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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(14.05.98), page 3, line 6 - line 10; claims X EP 0803348 A1 (ELF ATOCHEM S.A.), 29 October 1997 1-26 (29.10.97), abstract; column 1, line 14 - line 16; column 2, line 11 - line 25; claims X US 5840807 A (ALAIN FREY ET AL), 24 November 1998 1-26 (24.11.98), abstract; claims; column 2, line 10 line 16 X US 5888597 A (ALAIN FREY ET AL), 30 March 1999 1-26

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X	Further documents are list	ed in the continuation of Box (	C.	See patent family annex	κ.
•	Special categories of cited docume	mis	T-	later document published after the int	emational filing date or prior
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(30.03.99), abstract; claims

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Date of the actual completion of the international search	Date of mailing of the international search report
4 October 2000	1 6 -10- 2000
Name and mailing address of the ISA/	Authorized officer
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International application No.
PCT/FI 00/00487

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PCT/FI 00/00487

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- (81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- With international search report.
- With amended claims.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BREATHABLE THERMOPLASTIC POLYMER CASING FOR THE MANUFACTURE OF MEAT PRODUCTS

(57) Abstract: The invention relates to a food casing and more particularly to a breathable polymer food casing for the manufacture of meat products, such as dry sausages and cooked sausages and to a method for the manufacture thereof. Additionally, the invention relates to the use of a film or casing which is permeable to water vapour for dehydrating and/or maturing and/or smoking of meat products and more particularly to the use of films which are permeable to water and gases and which are continuous, that is to say which do not comprise perforations. The casing and/or film comprises thermoplastic polymer having polyether chains and with a moisture vapour transmission rate (MVTR) of equal or more than 150 g/m²/24 hours measured by the ASTM E96 BW method.

International application No.

PCT/FI 00/00487

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08J 5/18, A22C 13/00
According to International Patent Classification (IPC) or to both national classification and IPC

### **B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

### IPC7: C08J, A22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

### SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## B51, WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9819551 A1 (KALLE NALO GMBH), 14 May 1998 (14.05.98), page 3, line 6 - line 10; claims	1-26
x	EP 0803348 A1 (ELF ATOCHEM S.A.), 29 October 1997 (29.10.97), abstract; column 1, line 14 - line 16; column 2, line 11 - line 25; claims	1-26
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Dat	e of the actual completion of the international search	Date of mailing of the international search report		
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International application No.
PCT/FI 00/00487

ategory*	Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No
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International application No.
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